Unsaturated aliphatic C9-aldehydes as natural flavorants

(E)-2-Nonenal

By Jozef Kula and Halina Sadowska, Institute of General Food Chemistry, Technical University of Lodz, Poland

With its fatty, tallow and green odor strength, (E)-2-nonenal is an important component of natural flavors. Flavor experts describe it as having a rather unpleasant, rancid fat aroma when tasted at conventional flavor concentrations of 50 ppm or higher. But at extremely low concentration (in the range of 0.05-20 ppb) it produces a woody flavor which is very useful for enhancing the food aroma.

(E)-2-Nonenal is one of the commercially available unsaturated C9-aldehydes manufactured synthetically. The physicochemical and spectral data of the aldehyde are given in Table I.

Its relatively low threshold value of detection, 0.08-0.1 ppb,[1,2] gives it an advantage over other compounds that have to be used as flavor components at considerably higher concentrations. Such a woody type of flavor is especially desirable for flavor enhancement of coffee-flavored foodstuffs.[3] (E)-2-Nonenal can also be employed to contribute a slightly woody flavor to foods such as ice cream, boiled sweets, hard candy, meat products, milk drinks, cola and other beverages, both carbonated and non-carbonated.

This aldehyde exhibits some biological activity, being a component of the defense secretion of the tenebrinoid beetle (*Elodes beameric*).[4] It is also an attractant to olive

Table I. Physicochemical and spectral data of (E)-2-nonenal

$C_9H_{16}O$ **MW 140.23**

Boiling Point (°C/Torr)	Refractive Index (n_D^{20})	Density (d) (g/mL)	Infrared (cm^{-1})	^{1}H-NMR (δ)	Reference
88-90/12	1.4531	$0.846\,\frac{20}{4}$	-	-	24, 25
			2940,2740,1690 890, 715		30
				9.51 (d, J=7.6 Hz, 1H, CHO), 6.8 (dt, J=15.6 and 6.6 Hz, 1H, C3-H), 6.12 (ddt, J=15.6, 7.6 and 1.3 Hz, 1H, C2-H), 2.36 (m, 2H, C4-H), 1.32 (m, 8H), 0.89 (t, J=5.5 Hz, 3H, CH_3)	9, 27

NMR = Nuclear Magnetic Resonance

This is the last of three articles by Kula and Sadowska on the unsaturated aliphatic C9-aldehydes as natural flavorants. Previous articles discussed (E,Z)-2,6-Nonadienal (September/October 1993) and (E,E)-2,4-Nonadienal (November/December 1993).

0272-2666/94/0002-0051$04.00/0—

fruit flies[5] and the saw-toothed green beetle.[6] It was shown by Scriven[7] to be a repellent to the cockroach (*Periplaneta americana*). The aldehyde is also used for pretreatment of wheat for protection from fungal infection.[8]

Occurrence

Unsaturated fatty acids such as linoleic acid[9] or arachidonic acid[10] are precursors for the 2-nonenal formation in enzymatic and nonenzymatic processes. Thus, this aldehyde can be encountered in both plant and animal products. It was proved that (E)-2-nonenal shares responsibility for the specific flavor of fresh cucumbers where it occurs with (E,Z)-2,6-nonadienal.[11,12] More recent analytical studies reveal that this compound is a microcomponent of a great many plants which are consumed by man.[13] Suffice it to mention that the aldehyde is an ingredient of the volatile parts of popcorn,[14] rice[15] and apricot.[16] It is a constituent of volatiles of non-smoked beef, pork and chicken.[17] A study of fish has demonstrated that lipoxygenase in the gill tissue has the potential to be an important initiator of lipid oxidation and can generate 2-nonenal and other oxidative volatile compounds.[18]

Synthesis

A number of elaborate syntheses have been reported for (E)-2-nonenal. The methods employ such raw materials as 2-nonenol, nonanal, heptanal and castor oil.

Oxidation of 2-nonenal with chromic acid anhydride[19,20] produces this aldehyde in a high yield but the process is suitable only for the laboratory. Bedoukian,[21] starting from an easily available nonanal, synthesized (E)-2-nonenal in a five-step procedure (Figure 1).

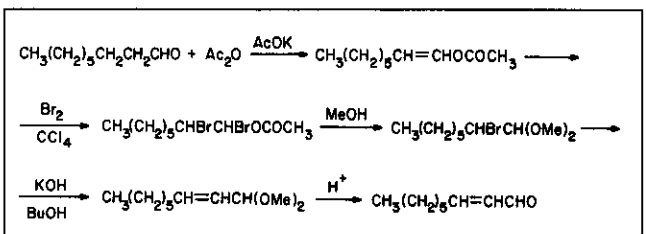

Figure 1. Transformation of saturated aldehydes into α,β-unsaturated ones[21]

The most important substrate material for the preparation of (E)-2-nonenal seems to be heptaldehyde. Thus, Makin[22] prepared this aldehyde by condensing ethylvinyl ether with heptanal diethylacetal and subsequent hydrolysis (Figure 2).

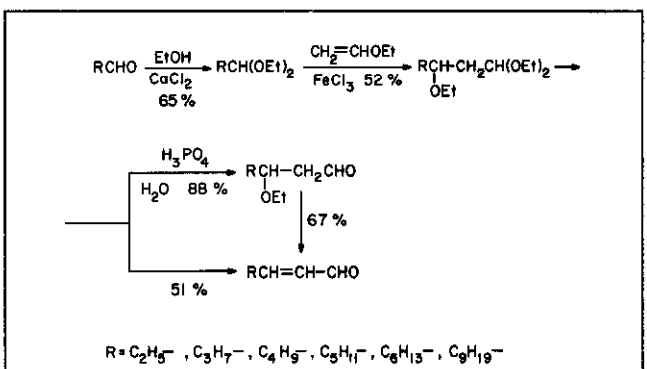

Figure 2. Formation of α,β-unsaturated aldehydes according to Makin[22]

A U.S. patent[3] gives some details on how to manufacture this aldehyde from heptanal (Figure 3).

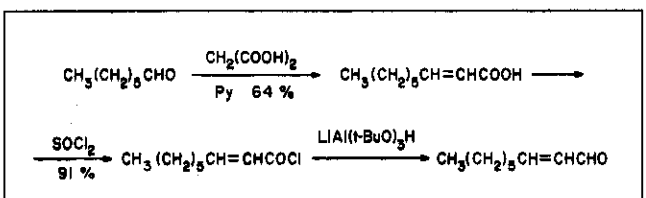

Figure 3. Synthesis of (E)-2-nonenal from n-heptanal[3]

A similar series of reactions for the synthesis (E)-2-nonenal is reported by Gadkari[23] (Figure 4). The method employs a convenient reducing agent, bis(triphenylphosphine)-copper tetrahydroborate, for transformation of the intermediate acid chloride into the aldehyde.

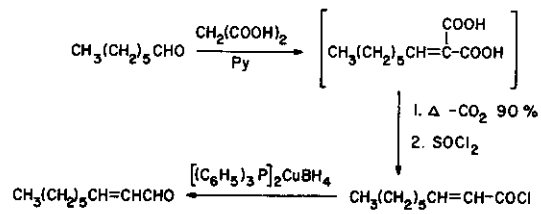

Figure 4. Synthesis (E)-2-nonenal from heptaldehyde according to Gadkari[23]

The Wittig reaction may be a good manner for the production of (E)-2-nonenal from heptaldehyde, but the preparation of the Wittig agent and the isolation of the product is tedious (Figure 5).[24,25]

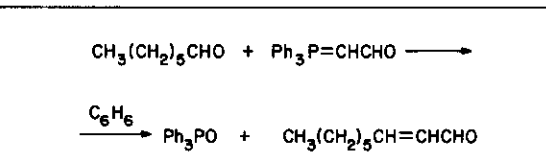

Figure 5. Obtaining 2-nonenal in Wittig reaction[24, 25]

Castor oil, containing ca. 90% of ricinoleic acid glyceride, is a promising raw material for the production of (E)-2-nonenal. More than 50 years ago Swern[26] reported that the hydroxylation of castor oil by hydrogen peroxide led to a trihydroxy derivative which, after treating with lead tetraacetate, furnished 2-nonenal with overall yield of 24%.

We have developed a new method for the synthesis of (E)-2-nonenal from castor oil (Figure 6).[27] This one-pot synthesis is based on the ozonolysis of castor oil in acetic acid followed by dehydration of the intermediate hydroxy aldehyde. Overall yield of the process is ca. 30% and the product obtained is of high purity.

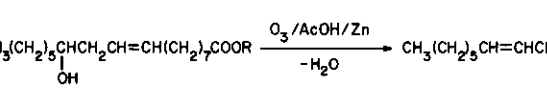

Figure 6. One-pot synthesis of (E)-2-nonenal from castor oil[27]

A few more, rather sophisticated syntheses of 2-nonenal[28-30] have been reported, but they are of low practical importance.

It is worth noting that 2-nonenal is also used for the preparation of other aroma compounds which are utilized for foodstuff flavoring. For example, its acetals[3] and 1,1,3-trialkoxynonanes[31] are valuable compounds balancing and blending the natural flavor of some food and beverages.

Summary

(E)-2-Nonenal is an interesting flavor compound which, at extremely low concentration, exhibits its useful odor and flavor properties. The aldehyde also demonstrates a biological activity. The reported syntheses of 2-nonenal are mostly multi-stage and research on simplifying this compound's synthesis should be continued.

References

Address correspondence to Dr. Jozef Kula, Institute of General Food Chemistry, Technical University of Lodz, ul. Stefanowskiego 4/10, 90-924 Lodz, Poland.

1. RG Buttery, RM Seifert, DG Guadagni, DR Black and LC Ling, *J Agric Food Chem* **16** 1009 (1968)
2. MH Boehlens and J van Gemert, *Perf & Flav* **12**(5) 31 (1987)
3. US Pat 3,962,321, TH Parliment et al (1976); *Chem Abstr* **85** 159432 (1976)
4. WR Tschinkel, *J Insect Physiol* **21** 753 (1975)
5. PM Guerin, U Remund, EF Boller, B Katsoyannos and G Delrio, *Comm Eur Communities (Rep) Eur 8384* (1983) pp 248-251; *Chem Abstr* **99** 173356 (1984)
6. KL Mikolajczak, BW Zilkowski, CR Smith and WE Burkholder Jr, *J Chem Ecol* **10** 301 (1984)
7. R Scriven and CE Meloan, *Ohio J Sci* **84** 82 (1984); *Chem Abstr* **101** 124825 (1984)
8. B Nandi, *Cereal Chem* **55** 121 (1978); *Chem Abstr* **89** 4732 (1978)
9. F Urlich and W Grosch, *Fat Sci Technol* **90** 332 (1988)
10. DB Josephson, RC Lindsay and DA Stuiber, *J Agric Food Chem* **32** 1344 (1984)
11. W Grosch and HD Bleitz, *Naturwissenschaften* **65** 58 (1978)
12. P Schieberle, S Ofner and W Grosch, *J Food Sci* **55** 193 (1990)
13. *Volatile Compounds in Food, Supplement 3,* H Maarse and CA Vischer, eds, Zeist, The Netherlands: TNO-BCI (1992)
14. P Schieberle, *J Agric Food Chem* **39** 1143 (1991)
15. RG Buttery, JG Turnbaugh and LC Ling, *J Agric Food Chem* **36** 1006 (1988)
16. GR Takeoka, RA Flath, TR Mon, R Teranishi and M Guentert, *J Agric Food Chem* **38** 474 (1990)
17. N Ramarathnam, LJ Rubin and LL Diosady, *J Agric Food Chem* **39** 1845 (1991)
18. RJ Hsieh and JE Kinsela, *J Agric Food Chem* **37** 279 (1989)
19. W Surber, O Theus, L Colombi and H Schinz, *Helv Chim Acta* **39** 1299 (1956)
20. FS Guzia and FA Luzzio, *J Org Chem* **47** 1787 (1982)
21. PZ Bedoukian, *J Am Chem Soc* **79** 889 (1957)
22. SM Makin, SM Gabrelyan and AS Chebotarer, *Zh Org Khim* **10** 2040 (1974)
23. RG Gadkari and AH Kapadi, *Biovigyanam* **15** 111 (1989)
24. BS Trippett and DM Walker, *Chem Ind* 202 (1960)
25. TM Cresp, MV Sargent and P Vogel, *J Chem Soc Perkin Trans* **1** 37 (1974)
26. JT Scalan and D Swern, *J Am Chem Soc* **62** 2309 (1940)
27. J Kula and H Sadowska, *J Am Oil Chem Soc* **70** (6) 643-644 (1993)
28. G Gamboni and H Shinz, *Helv Chim Acta* **41** 1603 (1958)
29. Ma Dawei and Lu Xiyan, *J Chem Soc Chem Commun* 890 (1989)
30. P de Shong and JM Leginus, *J Org Chem* **49** 3421 (1984)
31. Ger Offen 2162720, MF Epstein, assigned to General Foods Corp (Oct 12, 1972); *Chem Abstr* **78** 3707 (1973)